

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S UNIVERSITY]

## The Cobalt Ammine Salts of 12-Molybdophosphoric Acid

BY HAROLD A. HORAN

The recent work of Keggin and others<sup>1</sup> has shown that many salts of 12-molybdophosphoric acid are derived from the anion  $\text{PMO}_{12}\text{O}_{40}^{-3}$ . The structures of the alkali and ammonium salts have been determined and in general the composition of the anhydrous salts may be represented as  $\text{M}_3\text{PMO}_{12}\text{O}_{40}$  while the hydrates have the composition  $\text{M}_3\text{PMO}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$ . Many salts of this heteropolyacid with the alkaline earth and heavier metals are known.<sup>2</sup> With the divalent cations the salts generally may be represented by  $\text{M}_3(\text{PMO}_{12}\text{O}_{40})_2 \cdot x\text{H}_2\text{O}$ , while the salts involving the trivalent cations conform to the general formula  $\text{M}(\text{PMO}_{12}\text{O}_{40}) \cdot x\text{H}_2\text{O}$ .

The complex cations of the cobaltic and chromic ammine series form characteristic precipitates with 12-molybdophosphoric acid.<sup>3,4</sup> The compositions of these salts have not in general been determined. By analogy to the simple cations we would expect a trivalent complex cation such as the hexammine cobaltic ion to form a salt of the type  $[\text{Co}(\text{NH}_3)_6]\text{PMO}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ . With the divalent complex cations of the pentammine series we would expect a salt such as  $[\text{Co}(\text{NH}_3)_5\text{X}]_2(\text{PMO}_{12}\text{O}_{40})_2 \cdot x\text{H}_2\text{O}$ , where X is Cl, Br,  $\text{NO}_3$ , etc.

The precipitation of the nitratopentammine salt of 12-molybdophosphoric acid has been proposed for the gravimetric determination of phosphates<sup>4</sup> and as a result of a partial analysis of the salt the formula  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{HPMO}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}$ <sup>5</sup> was suggested. This would indicate salts of the type  $[\text{Co}(\text{NH}_3)_5\text{X}](\text{HPMO}_{12}\text{O}_{40})$ , where X is Cl, Br,  $\text{NO}_3$ , etc. These would be acid salts of the acid,  $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ . Acid salts of this acid involving the simple mono and divalent cations do not exist.

It is known that the pentammine cations undergo reaction in aqueous solution,<sup>6</sup> namely

(1) Keggin, *Proc. Roy. Soc. (London)*, **144A**, 75 (1934); Bradley and Illingworth, *ibid.*, **157A**, 113 (1936); Santos, *ibid.*, **150A**, 309 (1935); Illingworth and Keggin, *J. Chem. Soc.*, 575 (1935).

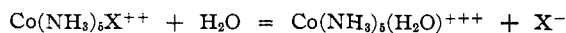
(2) Mellor, "Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol. XI, Longmans Green & Co., London, 1931, p. 663.

(3) Ephraim-Thorne, "Textbook of Inorganic Chemistry," 2d ed., Gurney and Jackson, London, 1934, p. 441.

(4) Furman and State, *Ind. Eng. Chem., Anal. Ed.*, **8**, 420 (1936).

(5) The type expected of a divalent cation  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]_2(\text{PMO}_{12}\text{O}_{40})_2$ , was eliminated as a result of the analysis. See H. M. State, Dissertation, Princeton University, 1936.

(6) Lamb and Marden, *THIS JOURNAL*, **33**, 1873 (1911); Lamb and Fairhall, *ibid.*, **45**, 378 (1923).



The rate and extent of this reaction depend, among other factors, on what X is. Evidence will be presented in this paper to show that due to this reaction the salts formed with the various pentammine cations and 12-molybdophosphate are all of the same composition, namely,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{PMO}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ . The normal or acid salts mentioned above are not formed. Probably the size of the cation involved is a determining factor in the formation of normal salts of the type,  $\text{M}_3(\text{PMO}_{12}\text{O}_{40})_2$ , and with large complex cations this structure cannot build up. As for acid salts there is no reason to expect these with the complex cations any more than with the simple ones.

Evidence will also be presented to show that the salt formed with the hexammine cobaltic ion may be represented as  $\text{Co}(\text{NH}_3)_6(\text{PMO}_{12}\text{O}_{40}) \cdot 3\text{H}_2\text{O}$ . It is probable in both cases that part or all of the water of crystallization is lattice water.<sup>7</sup>

## Experimental

**Materials.**—Chloropentammine, aquapentammine and hexammine cobaltic chlorides were prepared and purified by the methods of Biltz.<sup>8</sup> After purification, the salts were washed free of hydrochloric acid with 95% alcohol and finally with small portions of ether. The aquapentammine was air dried, while the chloropentammine and hexammine were dried in an oven, the former at 60° and the latter at 130°. The composition and purity were checked in all cases by Kjeldahl ammonia determinations, and in addition by gravimetric chloride determinations in the case of the aquapentammine and hexammine chlorides. The results were: calcd. for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ :  $\text{NH}_3$ , 34.00. Found:  $\text{NH}_3$ , 34.15. Calcd. for  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ :  $\text{NH}_3$ , 31.72; Cl, 39.62. Found:  $\text{NH}_3$ , 31.80; Cl, 39.69. Calcd. for  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ :  $\text{NH}_3$ , 38.20; Cl, 39.76. Found:  $\text{NH}_3$ , 38.29; Cl, 39.68.

The nitratopentammine cobaltic nitrate was prepared by the method of Jørgensen.<sup>9</sup> After purification, it was washed thoroughly with 95% alcohol and then with ether. It was dried in an oven at 50°. It was analyzed for ammonia and total ammonia plus nitrate, the former being done by Kjeldahl and the latter by a modified Kjeldahl method.<sup>10</sup> Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$ :

(7) Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., New York, 1938, p. 164.

(8) Biltz, "Laboratory Methods of Inorganic Chemistry," Hall and Blanchard, John Wiley and Sons, Inc., New York, 1909, pp. 173-177.

(9) Jørgensen, *J. prakt. Chem.*, [2] **23**, 227 (1881).

(10) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, 1936, p. 536.

NH<sub>3</sub>, 25.79; NH<sub>3</sub> + NO<sub>3</sub> as N, 33.95. Found: NH<sub>3</sub>, 25.70; N, 33.84.

Two standard phosphate solutions were employed. One was prepared and standardized by the method of Furman and State.<sup>4</sup> The other was prepared by weighing out a definite amount of twice recrystallized potassium dihydrogen phosphate (Merck reagent grade) which had been dried to constant weight at 100° and dissolving and making up to a definite volume. The phosphorus content of this solution was checked by double precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate. These solutions will be designated as A and B, respectively. Solution A contained 0.2956 mg. of phosphorus per ml. and solution B contained 0.3196 mg. of phosphorus per ml.

Acid sodium molybdate was prepared immediately prior to use according to Furman and State,<sup>4</sup> using Merck reagent grade molybdic acid. This solution is approximately 1.4 molar.

The potassium permanganate solution used in the molybdenum determinations was standardized against the best obtainable sodium oxalate.

The ferric alum used in the molybdenum determinations was Merck reagent grade. A blank on this and the Jones reductor used was quite small and consistent, 0.10–0.12 ml. of 0.1 *N* potassium permanganate.

The sulfuric acid and sodium hydroxide used were the ordinary *c. p.* reagents.

**Precipitations.**—The precipitates were formed, filtered, washed and dried according to the directions of Furman and State.<sup>4</sup> The above-mentioned pentammines were used as precipitants. Solutions of these were prepared immediately prior to use and were approximately 0.025 molar in all cases.

The procedure follows. To the phosphate contained in a volume of approximately 8 ml. and free of nitric and hydrochloric acids but containing approximately 36 milliequivalents of sulfuric acid add 1 ml. of acid sodium molybdate solution for each milligram of phosphorus present. After heating the solution to near boiling, slowly add the pentammine solution. The rates of formation of precipitates increased in the order chloropentammine, nitratopentammine, aquapentammine. This is in agreement with known rates of conversion of the acido ions to the aquapentammine ion. Sufficient precipitant was added in all cases to color the supernatant liquid pink and then an excess of 2–3 ml. in the aqua and nitrate cases. Complete precipitation could not be obtained in the case of the chloropentammine unless an excess of 6–8 ml. of precipitant was used. In all cases the solutions were kept near the boiling point for five to ten minutes to ensure complete precipitation. Longer digestion, fifteen to twenty minutes, was found necessary in the case of the chloropentammine. The volume of solution in all cases was approximately 20 ml. After cooling to room temperature the solutions were filtered through a porous porcelain crucible. The precipitates were washed free of sulfuric acid with 0.3 *N* nitric acid and then once with a small portion of water. The crucibles and contents were washed with 95% alcohol followed by ether. Air was drawn through the crucible for five minutes. The outside of the crucible was wiped with a lintless cloth and the

former was placed in an evacuated desiccator over calcium chloride. The crucibles were weighed after thirty minutes. The results of some of the precipitations with the pentammine reagents are given in Table I.

Precipitations were carried out in a similar manner using hexammine cobaltic chloride as the precipitant. This solution was made up approximately 0.025 molar. It was found necessary in these cases to double the amount of sulfuric acid present in order to prevent the precipitation of the molybdate of the ammine. A small excess, 2–3 ml., of precipitant beyond that necessary to color the supernatant liquid orange was used. Table II contains the results of precipitations with the hexammine reagent.

The theoretical weights of precipitate according to the proposed formula for the cobaltic aquapentammine molybdophosphate are given in Table I. Similar data are given in Table II for cobaltic hexammine molybdophosphate.

TABLE I  
PRECIPITATIONS OF 12-MOLYBDOPHOSPHATE WITH  
COBALTIC PENTAMMINE SALTS

Standard soln. used	Volume taken, ml.	Phosphorus taken, mg.	Precipitant used	Wt. of ppt., g.	Theoretical wt., <sup>a</sup> g.
A	10.01	2.959	Aqua	0.1970	0.1965
A	10.01	2.959	Nitrato	.1961	.1965 <sup>b</sup>
A	10.01	2.959	Chloro	.1966	.1965
A	25.01	7.393	Aqua	.4914	.4909
A	25.01	7.393	Nitrato	.4907	.4909 <sup>b</sup>
A	25.01	7.393	Chloro	.4901	.4909
B	25.01	7.993	Aqua	.5294	.5307
B	25.01	7.993	Nitrato	.5300	.5307 <sup>b</sup>
B	25.01	7.993	Chloro	.5280	.5307
A	49.98	14.77	Aqua	.9790	.9810
A	49.98	14.77	Nitrato	.9795	.9810 <sup>b</sup>

<sup>a</sup> The theoretical values are calculated from the amount of phosphorus taken and the formula [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]-PMO<sub>12</sub>O<sub>40</sub>·4H<sub>2</sub>O. <sup>b</sup> The theoretical values in these cases according to the formula proposed by Furman and State<sup>4</sup> are, respectively, 0.1956, 0.4886, 0.5283, 0.9764.

TABLE II  
PRECIPITATIONS OF 12-MOLYBDOPHOSPHATE WITH  
COBALTIC HEXAMMINE CHLORIDE

Standard soln. used	Volume taken, ml.	Phosphorus taken, mg.	Wt. of ppt., g.	Theoretical wt., <sup>a</sup> g.
B	4.98	1.592	0.1043	0.1047
B	4.98	1.592	.1051	.1047
B	10.01	3.199	.2109	.2105
B	10.01	3.199	.2107	.2105
B	25.01	7.993	.5263	.5258
B	25.01	7.993	.5271	.5258
B	49.98	15.97	1.055	1.051
B	49.98	15.97	1.057	1.051

<sup>a</sup> The theoretical values are calculated from the amount of phosphorus taken and the formula [Co(NH<sub>3</sub>)<sub>6</sub>]PMO<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O.

**Method of Analysis of Precipitates.**—Samples for analysis were prepared and dried as mentioned above. Ammonia was determined by distillation from a sodium hydroxide solution into an excess of standard hydrochloric

acid, the excess being titrated with standard sodium hydroxide using methyl red as an indicator.

In the case of precipitates formed using the nitratopentammine reagent, total ammonia plus nitrate determinations were carried out using a modified Kjeldahl method.<sup>10</sup> This method was tested successfully on samples composed of pure potassium nitrate and the molybdophosphate precipitated with the aquapentammine reagent, the combined ammonia and nitrate value being known in these samples.

Molybdenum was determined in samples which were dissolved in a minimum of sodium hydroxide solution and warmed until all ammonia had been expelled. The cobaltic hydroxide thus formed dissolved on the addition of 10 ml. of concentrated sulfuric acid. The solution was evaporated to the fumes of sulfur trioxide and fumed for three to five minutes. This served to destroy any hydrogen peroxide, nitrate and chloride. After dilution the solution was passed through a Jones reductor and the reduced solution was caught under an excess (5-fold) of ferric alum. After the addition of a few ml. of phosphoric acid the solution was titrated with standard potassium permanganate solution. A blank was run on all reagents, including appropriate amounts of cobalt and phosphorus, and the proper correction made. This was never more than 0.12 ml. of 0.1 *N* potassium permanganate solution.

Cobalt and phosphorus determinations were not carried out since the amounts of these constituents are so small that nothing definite would be established by them. Furman and State<sup>4</sup> determined these constituents in the precipitate formed with the nitratopentammine reagent. Their values agree closely with the theoretical values of these constituents on the basis of the formula proposed above for the aquapentammine molybdophosphate.

The precipitates formed using the aquapentammine and chloropentammine reagents were tested qualitatively for chloride. This constituent was found in small amounts. Its presence is probably due to occlusion or post-precipitation.

**Results of Analysis.**—Some typical results on the precipitate formed using the aquapentammine precipitant follow.<sup>11</sup> Found: NH<sub>3</sub>, 4.16, 4.18; Mo, 55.87, 55.91. For the precipitate formed using the nitratopentammine precipitant: Found: NH<sub>3</sub>, 4.15, 4.17; Mo, 56.05, 56.15; Total NH<sub>3</sub> + NO<sub>3</sub>, calcd. as NH<sub>3</sub>, 4.16, 4.17. For the precipitate formed using the chloropentammine precipitant: Found: NH<sub>3</sub>, 4.19, 4.17; Mo, 55.85, 56.03. The theoretical values according to the proposed formula for the aquapentammine molybdophosphate: calcd. for [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]PMo<sub>12</sub>O<sub>40</sub>·4H<sub>2</sub>O: NH<sub>3</sub>, 4.14; Mo, 55.99; Total N as NH<sub>3</sub>, 4.14.

With the precipitate formed using hexammine cobaltic chloride as the precipitant the following are some typical

results. Found: NH<sub>3</sub>, 4.96, 4.99; Mo, 56.46, 56.63. Calcd. for [Co(NH<sub>3</sub>)<sub>6</sub>]PMo<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O: NH<sub>3</sub>, 5.02; Mo, 56.51.

### Discussion<sup>11</sup>

The results of precipitations and analysis of the salt formed using the nitratopentammine reagent agree closely with those of Furman and State.<sup>4</sup> However, these authors did not determine total ammonia and nitrate and assumed the presence of the latter. The above analysis shows definitely the absence of nitrate. The above results also show definitely that the compound formed with the different pentammine reagents is always the same.

The hexammine and aquapentammine molybdophosphates are similar in composition. The former apparently has three moles of water of crystallization per mole of the salt, while the latter apparently has four. The direct determination of water is not reliable due to decomposition of the salts at temperatures sufficiently high to drive off all of this constituent. We would expect a close similarity between the two salts due to the similar structures of the cations, Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sup>+++</sup> and Co(NH<sub>3</sub>)<sub>6</sub><sup>+++</sup>.

The precipitation of phosphate in the form of such complex compounds is the basis of a satisfactory gravimetric determination of this constituent. Hexammine cobaltic chloride would seem to be the best precipitant. Furman and State<sup>4</sup> claim the nitratopentammine reagent gives the most satisfactory precipitate for analytical purposes. They mention the difficulty of filtering and washing the hexammine precipitate. This difficulty is not apparent except when dealing with very large amounts of precipitate, 1 g. or more, and in such cases the method is scarcely applicable. In view of the comparative ease of preparation and purification as well as stability of solutions, the hexammine precipitant would seem preferable to the nitratopentammine. An additional disadvantage of the nitratopentammine is its low solubility, approximately 8.5 g. per liter. This necessitates the use of large volumes of reagent in many cases, causing unnecessary dilution of the solution. The hexammine reagent easily can be made up ten times as strong as the nitrate reagent. The former has been used successfully in other gravimetric determinations.<sup>12,13</sup>

(11) During the progress of the work which Professor Horan reports in the present paper, he communicated his conclusions regarding the complete aquation of the nitratopentammine salt to us, and these were confirmed by one of us (H. M. S.) and forwarded to Dr. Horan in August of 1938. Although qualitative tests for nitrate may sometimes be obtained, State's quantitative estimations made in 1938 by the Devarda alloy reduction method and subsequent distillation of ammonia gave the same value for total nitrogen as did the direct distillation of the ammonia after adding alkali alone.—[N. H. FURMAN and H. M. STATE.]

(12) M. Parks, Dissertation, Columbia University, 1930.

(13) Hynes and others, *Ind. Eng. Chem., Anal. Ed.*, **8**, 356 (1936).

### Conclusions

The compositions of the cobaltic pentammine and hexammine salts of 12-molybdophosphoric acid have been determined. The divalent acid cations do not directly form salts with this acid but react with water forming a trivalent ion which then reacts with the molybdophosphate.

The compositions of the cobaltic hexammine molybdophosphate and the cobaltic aquapentammine molybdophosphate are quite similar.

Suggestions have been made concerning the use of hexammine cobaltic chloride as a reagent in the quantitative determination of phosphates.

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## The Protium-Deuterium Ratio and the Atomic Weight of Hydrogen

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On the basis of a protium-deuterium ratio in normal water<sup>1</sup> of 5000, the International Committee on Atomic Weights<sup>2</sup> recently changed the accepted atomic weight of hydrogen from 1.0078 to 1.0081; no reference to the source of this ratio, 5000, was given and the Committee apparently overlooked the work of Gabbard and Dole<sup>3</sup> who found 6900 and of Hall and Jones<sup>4</sup> who found 6500. It is the purpose of this paper to demonstrate by a new exchange reaction method the validity of the Gabbard-Dole ratio of 6900, and to point out that the chemical atomic weight of hydrogen is probably closer to 1.0080 than to 1.0081. At the same time we shall also reinvestigate the density of water made from atmospheric oxygen as compared to normal water inasmuch as the published data in the literature vary from 6.0 to 8.6 $\gamma$ <sup>5</sup> for this important constant of nature. We use methods presumably free of isotopic errors, or uncertainties inherent in electrolytic separation, in combustion, in dubious extrapolations or corrections to the data and in isotopic exchange equilibria which are functions of temperature. Furthermore, a modified float method of measuring densities sensitive to  $\pm 0.1 \gamma$  or better and improved techniques throughout increase the reliability of the final observations.

In principle the new method consists in the continued elimination of all the heavy hydrogen from normal water through repeated exchange reactions  $H_2 + HOD \rightleftharpoons HD + HOH$ , without af-

fecting the isotopic composition of the oxygen, until the density of the water has been reduced to a constant minimum value. From the  $\gamma$ -value of this water the protium-deuterium ratio in normal water can be calculated. By burning deuterium-free hydrogen in excess with oxygen of the air, the relative atomic weight of atmospheric oxygen can be calculated from the appropriate combination of the above data.

We have also measured the protium-deuterium ratio in Atlantic Ocean water in order to investigate the influence of the source of the water on this ratio.

### Experimental

**Preparation of Deuterium-free Water Containing Atmospheric Oxygen.**—The deuterium-free water which served as a source of D-free hydrogen was prepared by the fractional electrolysis of water using the cells of Gabbard and Dole.<sup>3</sup> The complete elimination of deuterium was proved by combining the hydrogen from each successive electrolysis with atmospheric oxygen, the hydrogen always being in excess, and by measuring the density of the resulting water. When a minimum value of the density had been attained, the water was assumed to be D-free. Data obtained in this work are given in Table I and plotted in Fig. 1, where the rapidity with which deuterium is eliminated by electrolytic fractionation (factor equal to 5.2) is readily seen. In this plot the diameter of the circles is twice as great as the experimental error.

TABLE I  
DATA FOR DENSITIES OF WATER MADE FROM HYDROGEN ON SUCCESSIVE ELECTROLYTIC FRACTIONATION AND ATMOSPHERIC OXYGEN

No. electrolytic fractionations	$\gamma$
1	-5.9
2	-7.5
3	-8.9
4	-8.9 $\pm$ 0.1
5 (Gabbard and Dole <sup>3</sup> )	-9.0 $\pm$ 0.3
4 (Hall and Jones <sup>4</sup> )	-8.9 $\pm$ 0.3

(1) We define the term "normal water" in this paper as signifying purified Lake Michigan water.

(2) G. P. Baxter, O. Hönlgschmid and P. LeBeau, *THIS JOURNAL*, **60**, 737 (1938).

(3) J. L. Gabbard and M. Dole, *ibid.*, **59**, 181 (1937). For references to earlier results see this paper.

(4) N. F. Hall and T. O. Jones, *ibid.*, **58**, 1915 (1936).

(5)  $\gamma$  is defined as the excess density of the water in question over that of normal water in parts per million. A negative sign for  $\gamma$  means that the water is lighter than normal.